MISSOURI DEPARTMENT OF NATURAL RESOURCES
AIR AND LAND PROTECTION DIVISION
ENVIRONMENTAL SERVICES PROGRAM
Standard Operating Procedures

SOP #: MDNR-WQMS-114 EFFECTIVE DATE: June 2, 2003

SOP TITLE: Determination of Time-of-Travel in Streams Using a Turner Designs Field Fluorometer

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SUMMARY OF REVISIONS: Minor changes have been made in this document to reflect equipment updates and expanded monitoring duties. Document was reformatted.

APPLICABILITY: The procedures described in this SOP are applicable to all ESP personnel involved with water quality studies and associated hydrologic investigations.

DISTRIBUTION: MoDNR Intranet
ESP SOP Coordinator

RECERTIFICATION RECORD:

Date Reviewed				
Initials				

1.0 SCOPE AND APPLICABILITY

Hydrological studies are a major part of many water quality surveys conducted by the Water Quality Monitoring Section (WQMS) of the Environmental Services Program (ESP). These studies can include a variety of activities such as flow measurement, dye dilution for extent of mixing zone area, and time-of-travel studies. This Standard Operating Procedure (SOP) deals specifically with time-of-travel studies. Time-of-travel studies can give modelers and planners important data for model calibration and Total Maximum Daily Load (TMDL) calculations.

2.0 SUMMARY OF METHOD

There are three principle methods of determining time-of-travel in streams: floating an orange or other buoyant item on the water surface for a given distance, using a flow meter and measuring tape for determining velocities across a stream channel, and following and measuring a tracer such as dye.

The use of dye as a tracer is the most accurate method of measuring time-of-travel through a stream segment. The WQMS uses a non-toxic water-soluble dye (Rhodamine WT) when conducting time-of-travel studies. The dye is injected into the stream and grab samples are collected at various intervals from a series of downstream locations. The samples are analyzed using a fluorometer to determine the concentration. The dye can be detected at concentrations as low as 0.01 ppb (parts per billion). The concentrations are plotted against time and distance traveled. The resulting time-concentration curve is the basis for determining time-of-travel characteristics of streams.

3.0 HEALTH AND SAFETY REQUIREMENTS

3.1. Personnel who sample wastewater or surface water of unknown origin are encouraged to use the appropriate level of personal protective equipment (such as clean disposable rubber gloves and rubber boots) to protect themselves from waterborne illnesses when conducting field activities.

3.2. Personnel should participate in medical monitoring in accordance with the MDNR Division's medical monitoring policy. All field personnel who are routinely exposed to wastewater should be familiar with the hepatitis A prevention vaccine policy.

4.0 PERSONNEL QUALIFICATIONS

Field personnel shall have a working knowledge of field sample collection procedures and all applicable standard operating procedures. Staff should also be very familiar with the use of discrete sequential automatic samplers (ISCO models 1680, 2700, 2900, or 6700) and the Turner Designs model 10-005R field fluorometer. See MDNR-FSS-201 and MDNR-FSS-202 for further information.

5.0 SUPPLIES AND EQUIPMENT

5.1. Rhodamine WT is the water-soluble dye used by the WQMS for time-of-travel studies. The dye is non-toxic, fluorescent, highly detectable, reasonably stable, and has very low absorption and adsorption characteristics. The dye can be readily purchased through scientific supply companies in several forms: liquid, powder, or tablet. The liquid form is the most commonly used by WQMS personnel when conducting time-of-travel studies.

5.2. Dye injection equipment should include a 500 or 1000 mL graduated cylinder, funnel, disposable rubber gloves, waders or hip boots, and plastic trash bags. If the approximate amount of dye needed has been determined beforehand, then it is usually more convenient to pour the needed volume into a leak proof plastic container at the laboratory.

5.3. Sampling equipment should include the required number of ISCO discrete sequential samplers (for each sampling location), appropriate sampler bottles, Tygon tubing, strainers, batteries, and a minimum of 24 numbered glass vials with caps for each day of discrete automatic sampling at each stream location. Eight dram or one ounce size are convenient for collection purposes. In addition, marking pens, masking tape, and a storage container should be included.

5.4. The WQMS utilizes a Turner Designs model 10-005R field fluorometer for detecting the concentrations of dye recovered from the stream samples. The fluorometer can utilize either an AC or DC power source. Glass cuvettes are used to hold the sample portion used in the fluorometric analysis. In addition, time-of-travel data sheets are required to record the results of each analysis.

6.0 PROCEDURES

6.1. Generally, time-of-travel studies are conducted by the WQMS as part of waste load allocation studies requested by the Water Pollution Control Program (WPCP). Extensive planning is required before implementing a time-of-travel study. Topographic maps are valuable for determining general surface features of the stream: relief, impoundments, tributaries, land use, bridges, and other access points. A detailed study of the area will aid in selecting the appropriate locations and number of sampling locations.

6.2. A reconnaissance of the selected stream must be made prior to the implementation of the time-of-travel study. A thorough check of all potential sampling locations, including the wastewater treatment plant (WWTP), should be made and all notes recorded in a bound field notebook

6.2.1. The sampling schedule employed and dye quantity needed require estimates of velocity and travel time for each reach. Estimates of the channel width, depth, and velocity are necessary to get a general idea of the volume of dye required. Stream velocity can be estimated by floating an object and timing its travel with a stopwatch down a reach of stream of known length (oranges work well as floats; plan on using several, as some will probably be caught on snags or otherwise lost.) Try to estimate the velocity through a reach that includes both slower and faster flowing sections. Also, remember that estimated velocities in channels will usually be much higher than the actual velocity of the reach.

6.2.2 Inspect the site for dye injection and all proposed downstream sampling locations for accessibility. If the study area contains a WWTP, arrange to meet with the plant operator.

6.2.3 Check all stream reaches for dams, outfalls, diversions or other conditions that may affect discharge and mean velocity.

6.2.4 Determine suitable areas for conducting discharge measurements at the injection and each downstream sampling location. See SOP MDNR-WQMS-113*, Flow Measurements in Open Channels.*

6.2.5 Using estimates from the above observations, calculate the likely discharge at the last sampling station to compute the volume of dye needed. That is, the maximum discharge in the reach is used to estimate the amount of dye required.

6.3 The amount of dye required for a time-of-travel study is somewhat subjective and dependent on the experience of the investigator. Following are two methods for determination of Rhodamine WT dye required for a single slug injection:

- In general, it has been the experience of WQMS personnel that between 0.5 and 1.0 L of dye is a sufficient quantity for travel-time studies in streams having a discharge of less than 30 cubic feet per second (cfs).

- The following formula as recommended by the United States Geological Survey (USGS) can also be used to estimate dye requirements for Rhodamine WT dye:

  $V=2.0 \times 10^{-3} \ (QmL/v)^{0.93} Cp$, where V is the volume of dye in liters,
  Qm is the maximum discharge in the reach in cubic meters per second, and
  L is the distance from injection to sampling point, in kilometers, v is the mean velocity, in meters per second, and Cp is the peak concentration in micrograms per liter.

Generally, Cp in the above equation will not need to exceed 10 ug/L in order to achieve the desired concentration for the fluorometer readings. See pp. 18-20 of the USGS publication *Measurement of Time-of-Travel and Dispersion in Streams by Dye Tracing,* Book 3, Chapter A9, Techniques of Water-Resources of the USGS, 1989.

6.3.1. The dye cloud should be sampled at a minimum of two sites downstream from the point of complete mixing to provide a good definition of travel-time. If the stream reach is excessively long and the velocity very slow, separate time-of-travel studies may have to be carried out within each subreach.

6.3.2 Estimates of initial sampling time, intervals between samples and duration of sampling are based on the estimated mean velocity and length of reaches between injection and sampling sites. In general, a conservative estimate of the arrival of the leading edge of the dye cloud is required in order that the centroid will be sampled.

6.3.3 Most dye sampling by the WQMS ranges from 15-30 minute intervals at stations near the injection site to 30 to 60 minute intervals further downstream. When good estimates of arrival of the dye cloud at the sampling station are not feasible, it is advisable to periodically collect and read dye samples in the field until the dye is detected. At that time, a discrete sequential automatic sampler can be set up to collect water at intervals which allow for the centroid of the dye cloud to be sampled.

6.4 Dye tracing studies can be complex and most require a detailed study plan. Often, proper implementation will require multiple injection sites, numerous sampling sites, and multiple personnel. Coordination between members of the sampling team requires detailed instructions for both equipment use and injection of dye.

7.0 STUDY IMPLEMENTATION

Once all study plans have been made, application for use of the dye must be made with the MDNR's Geological Survey and Resource Assessment Division (see Appendix, Figure 3). Information requested on the form includes: location of the receiving stream, injection point, type and quantity of dye to be used, and the purpose of the study. The application form can be completed and faxed to the Division office in Rolla for approval. Approval generally can be granted in a matter of days, providing the application form is complete. Notification must also be given to the MDNR's Environmental Emergency Response Section, within the Environmental Services Program, and to the appropriate Regional Director. Notice may also be given to the local Missouri Department of Conservation (MDC) agent and affected property owners.

Within 30 days of completion of the study, a water trace information sheet (see Appendix, Figure 4) must be completed and submitted to the Geological Survey and Resource Assessment Division (GSRAD). Both the application and information sheet can be found on the MDNR's intranet under the Environmental Geology section.

7.1 Prior to injection of the dye, control samples must be collected for background fluorescence at all sampling locations. The samples are necessary to compensate for the natural fluorescence when analyzing the stream samples with the fluorometer.

7.2 In time-of-travel studies that are part of waste load allocation studies, the dye is normally poured into the wastewater treatment plant discharge where the effluent enters the stream. The dye is poured from a leak-proof container directly into the center of flow. Disposable rubber gloves should be worn when pouring the dye.

7.3 After injecting the dye, rinse and cap the dye container and remove the disposable rubber gloves and place in a plastic trash bag. Seal the trash bag and store it away from sample vials and the fluorometer.

7.4 Record in a field notebook the amount of dye injected, the time injected and the location of injection.

7.5 Begin the collection of dye samples shortly before the leading edge of the dye is expected. When possible, an ISCO sequential composite sampler should be set at the selected sampling location to collect 24 single samples at a time interval calculated to sample the leading edge, peak, and trailing edge of the dye cloud. Periodic fluorometric checks of collected samples are recommended to insure the dye will be accurately sampled. Dye clouds having an exceptionally long travel time may require additional 24 hour sampling periods.

7.6 Stream discharge should be measured at all sampling locations. Ideally, stream discharge should be measured when dye is present at the sampling location. If this is not feasible, then discharge must be measured at each sampling site shortly before commencement of the dye sampling.

7.7 Stream discharge should also be determined immediately upstream of the wastewater treatment discharge (if the time-of-travel is related to a wasteload allocation study). This is important to determine the wastewater plant's contribution to the stream flow during the dye sampling, since the treatment plant will have variable flows during a 24 hour period.

8.0 SAMPLE ANALYSIS AND DATA PRESENTATION

8.1 Refer to SOP MDNR-FSS-202, *General Operating Procedures for the Turner Designs Field Fluorometer (Model 10-005R)*.

8.2 Before beginning the analysis of dye samples, zero the fluorometer using the background sample collected from the appropriate sampling site. Record the results of all samples from each sampling site on the Time-of-Travel Data Sheet (Appendix, Fig. 1).

8.3 Plot or graph the data from the Time-of-Travel Data Sheet (dye concentration of each sample against time) to create a time-concentration curve (see p.3, *Measurement of Time-of-Travel and Dispersion in Streams by Dye Tracing* and Appendix, Fig. 2).

8.4 On the time-concentration curve, label the time for the leading edge, peak concentration, centroid, and the trailing edge of the dye cloud.

8.4.1 The peak concentration is simply the time when the highest dye concentration was sampled.

8.4.2 The centroid is the point of mean mass or median of the dye cloud. It is calculated by finding the time when 50% of the dye has passed the sampling point. Because the trailing edge of the dye cloud drops off gradually, the dye concentration curve will be skewed to the right and the centroid will always occur shortly following the peak concentration.

8.5 If desired, the time-concentration curves for each subreach can be combined and graphically represented as a travel time-distance curve for the entire stream reach.

9.0 REFERENCES

- MDNR-WQMS-113, *Flow Measurement in Open Channels*
- MDNR-FSS-202, *General Operating Procedures for the Turner Designs Field Fluorometer (Model 10-005R)*
- MDNR-FSS-201, *Use, Cleaning, and Maintenance of ISCO Automatic Wastewater Samplers*
- *Measurement of Time-of-Travel and Dispersion in Streams by Dye Tracing*, Book 3, Chapter A9, Techniques of Water-Resources Investigations, U.S. Geological Survey, 1989 (Revision)

APPENDIX

Figures 1, 2, 3, and 4

Figure 1.

Time-of-travel study on: ____

Sampling Site: ____

Dye Injected at: ________________________________Time/Date:___________________

Amount Injected: _________________Type of Dye: _________________Conc. %: ______

Sampling Section Discharge: _______________CFS Width: _______Mean Depth: _______

Field Sampling and Analysis | Laboratory Analysis

Sample #	Sample Point	Sample Time	Fluor. Sens. 1X-100X	Fluorometer Readings				Corrected Readings				Rel. Dye Conc.
				1X	3X	10X	30X	1X	3X	10X	30X	

Figure 2.

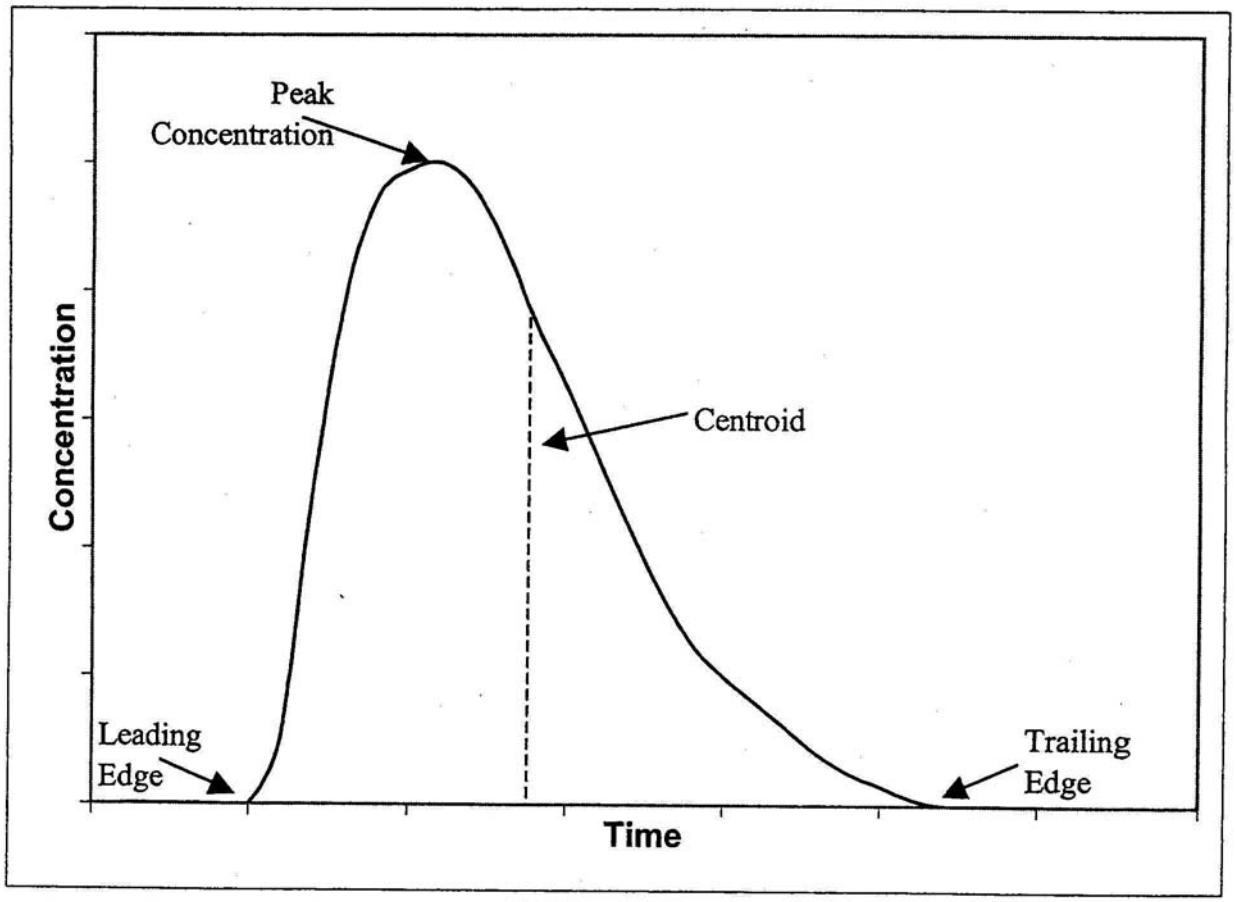
Peak
Concentration
Centroid
Concentration
Leading
Edge
Trailing
Edge
Time

Figure 3.

MISSOURI DEPARTMENT OF NATURAL RESOURCES
DIVISION OF GEOLOGY AND LAND SURVEY, GEOLOGICAL SURVEY PROGRAM
WATER TRACE INFORMATION SHEET
WATER TRACER REGISTRATION APPLICATION

FOR OFFICE USE ONLY	
REGISTRATION #	DATE RECEIVED
VARIANCE ☐ APPROVED ☐ DENIED	
BY	DATE

REGISTRANT'S INFORMATION

REGISTRANT'S NAME AND COMPANY		TELEPHONE	
ADDRESS	CITY	STATE	ZIP CODE

GENERAL INFORMATION

DESCRIPTION OF GENERAL TYPE(S) AND PURPOSE OF TRACE(S) TO BE UNDERTAKEN

LIST OF TRACERS WHICH MAY BE USED

IF VARIANCE FROM REGISTRATION IS DESIRED, PLEASE GIVE REASONS

COMMENTS

I HEREBY CERTIFY THAT THE ABOVE INFORMATION IS ACCURATE AND COMPLETE TO THE BEST OF MY KNOWLEDGE

REGISTRANT'S SIGNATURE	DATE

MO 780-1695 (12-98)

MAIL COMPLETED COPY TO: **DEPARTMENT OF NATURAL RESOURCES, ENVIRONMENTAL GEOLOGY SECTION, P.O. BOX 250, ROLLA, MO 65402-0250**
PHONE: (573) 368-2161 FAX: (573) 368-2111 E-MAIL ADDRESS: gspeg@mail.dnr.state.mo.us

Figure 4.

FOR OFFICE USE ONLY	
INJECTION POINT #	DATE RECEIVED
CHECKED BY	DATE
PLOTTED BY	DATE

MISSOURI DEPARTMENT OF NATURAL RESOURCES
DIVISION OF GEOLOGY AND LAND SURVEY, GEOLOGICAL SURVEY PROGRAM

WATER TRACE INFORMATION SHEET
INJECTION POINT

INJECTION POINT LOCATION

INJECTION POINT DESCRIPTION						COUNTY
¼ ¼ ¼ SECTION	¼ ¼ SECTION	¼ SECTION	SECTION	TOWNSHIP N.	RANGE E/W	QUADRANGLE NAME
WRITTEN LOCATION IF LEGAL DESCRIPTION IS UNAVAILABLE			PURPOSE OF TRACE			ELEVATION IN FEET

TYPE OF INJECTION POINT
☐ SEPTIC TANK ☐ WELL ☐ LAKE/POND ☐ SINKHOLE ☐ SEWER ☐ LAGOON ☐ STREAM ☐ OTHER _____

PROPERTY OWNER'S NAME			TELEPHONE	
ADDRESS	CITY		STATE	ZIP CODE

REGISTRANT'S INFORMATION

REGISTRANT'S NAME AND COMPANY			TELEPHONE	
REGISTRANT'S ADDRESS	CITY		STATE	ZIP CODE

INJECTION INFORMATION

	PROPOSED	ACTUAL		
INJECTION DATE _____	☐	☐	INJECTION TIME _____ A.M./P.M.	
TRACER INJECTED _____	☐	☐	NUMBER OF MONITORING POINTS _____	
TRACER AMOUNT _____	☐	☐		

FLOW CONDITIONS AT INJECTION

PLEASE INCLUDE A SKETCH MAP WITH THIS FORM!

A sketch map or photocopy of topographic map should contain the following: injection point, monitoring points, all known springs, sinkholes, caves, mines, and roads. Include a scale and north arrow on the sketch map.

COMMENTS

I HEREBY CERTIFY THAT THE ABOVE INFORMATION IS ACCURATE AND COMPLETE TO THE BEST OF MY KNOWLEDGE

REGISTRANT'S SIGNATURE	REGISTRATION NUMBER	DATE

MO 780-1693 (12-98)

MAIL COMPLETED COPY TO: **DEPARTMENT OF NATURAL RESOURCES, ENVIRONMENTAL GEOLOGY SECTION, P.O. BOX 250, ROLLA, MO 65402-0250**
PHONE: (573) 368-2161 FAX: (573) 368-2111 E-MAIL ADDRESS: gspeg@mail.dnr.state.mo.us